Ali Hafizi

Ali Ahmadpour[1]
e-mail: ahmadpour@um.ac.ir

Department of Chemical Engineering,
Faculty of Engineering,
Ferdowsi University of Mashhad,
Mashhad 9177948974, Iran

Majid M. Heravi
Department of Chemistry,
School of Sciences,
Alzahra University,
Tehran 1993893973, Iran

Fatemeh F. Bamoharram
Department of Chemistry,
School of Sciences,
Islamic Azad University,
Mashhad branch,
Mashhad 9187147578, Iran

Investigation of Silica-Supported Preyssler Nanoparticles as Nanocatalysts in Alkylation of Benzene With 1-Decene Using Artificial Intelligence Approach

Silica-supported Preyssler nanoparticles were synthesized and tested in alkylation of benzene with 1-decene. Adaptive network based fuzzy inference system (ANFIS) was successfully applied for studying the operating parameters of this catalytic reaction. The reaction was carried out at a constant temperature of 80 °C for 2 h, while catalyst loading, catalyst weight percent, and benzene to 1-decene molar ratio (Bz/C_{10}) were chosen as independent variables. Prediction of 1-decene conversion and linear alkylbenzene (LAB) production yield were performed by applying ANFIS method. The predictive ability and accuracy of ANFIS model were examined using unseen experimental data set and R^2 was obtained to be 0.994 and 0.995 for 1-decene conversion and LAB production yield, respectively. Experimental results revealed that catalyst loading, Bz/C_{10} molar ratio, and catalyst weight percent have positive effect on 1-decene conversion, while increase in catalyst loading tends to decrease LAB production yield.
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1 Introduction

Recently, because of the unique properties of nanoparticles, the application of them as catalysts has attracted much attention [1]. Catalysts, which are nanoparticles, are composed of clusters of atoms, often metals, with particle size varying between 1 and 20 nm [2]. As the particle size decreases, the relative number of surface atoms increases, and thus the activity increases [3]. In addition, nanometer-sized particles may show unique properties for several applications [4]. It is expected that nanostructured polyoxometalates show higher catalytic activity than any of the other micron-sized particles. This point is very important in catalysis reactions. In addition, nano-polyoxometalate compounds have several advantages as catalysts which make them economically and environmentally attractive [2].

In the recent years, interest has focused mainly on the synthesis of nanocatalysts such as the Keggin nanocatalysts. However, the synthesis and catalytic activity of the Preyssler nanocatalyst has not been studied extensively [3].

Alkylation of benzene with C_{10}–C_{14} linear alkenes is used for the synthesis of LAB. LAB is the primary raw material for the production of linear alkylbenzene sulfonates (LABS), which is a surfactant detergent intermediate [5].

Traditionally, LAB production is mostly based on homogeneous catalytic reaction with HF and $AlCl_3$ as catalysts [6]. Nonetheless, using these catalysts make many problems such as environmental pollution, equipment corrosion, safety, and separation difficulty. Owing to these problems of conventional catalysts, solid acid catalysts have been developed. Numerous materials have been evaluated as solid catalysts for this alkylation process [7–9].

The present study investigates the application of silica-supported Preyssler nanoparticles in the alkylation of benzene using ANFIS.

To the best of our knowledge, there is no report concerning the use of silica-supported Preyssler nanoparticles for the production of LAB. The other innovation of this paper is the use of ANFIS modeling for the investigation and prediction of reaction parameters on the catalyst performance of this nanocatalyst.

2 Modeling Description

Artificial neural network is a favorable technique to solve optimization problems because it can simulate the operations of the brain and use parallel processing to save computational time [10,11].

Fuzzy theory that was initiated by Lotfi Zadeh in 1965 [12] is a form of multivalued logic derived from fuzzy set theory. Recently, there has been a growing interest in combining both these methods. ANFIS model which is the combination of the neural network and the fuzzy logic approach, was initiated by Jang in 1993 [13]. This system implements the Takagi–Sugeno fuzzy inference system and had been used broadly in complex system identification and modeling of complex and nonlinear systems [13].

Assume that the examined fuzzy inference system has two inputs x_1 and x_2 and one output namely y. A typical rule based on Takagi–Sugeno fuzzy inference system with two rules can be expressed as

Rule#1: If x_1 is A_1; x_2 is B_1; Then: $y_1 = \alpha_1 x_1 + \beta_1 x_2 + \gamma_1$
Rule#2: If x_1 is A_2; x_2 is B_2; Then: $y_2 = \alpha_2 x_1 + \beta_2 x_2 + \gamma_2$

In which A_i and B_i ($i = 1, 2$) are fuzzy membership functions and y_i is the output of each rule while α_1, β_1, γ_1, α_2, β_2, and γ_2 are design parameters that are determined during the training process [14].

3 Experimental Method

3.1 Synthesis of Silica-Supported Preyssler Nanoparticles. The Preyssler's anion $[NaP_5W_{30}O_{120}]^{14-}$ was prepared according to the literatures [15,16]. $H_{14}[NaP_5W_{30}O_{110}]$ was prepared by the

[1]Corresponding author.

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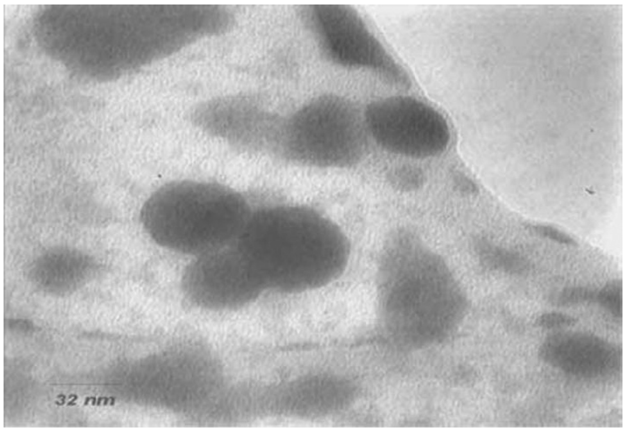

Fig. 1 TEM images of the synthesized nanostructures (the amorphous background structures are part of the TEM grid)

passage of a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50 W × 8 resin in the H^+ form and evaporation of the elute to dryness. Silica-supported Preyssler nanoparticles were prepared as indicated in our previous work [17].

3.2 Catalyst Characterization. Transmission electron microscopy (TEM) was applied for the characterization of the obtained nanostructure. The micrograph represented in Fig. 1 shows the morphology of silica-supported Preyssler nanoparticles. It indicates the spherical particles of silica-supported Preyssler nanoparticles with the diameter of about 30 nm.

3.3 Catalyst Testing. Liquid phase alkylation of benzene with 1-decene was carried out in an atmospheric pressure glass batch reactor equipped with a magnetic stirrer and a reflux condenser. The reactor was heated using a glass jacket and hot water. The reaction temperature was 80 °C with typical reaction time of 2 h. Silica-supported $H_{14}[NaP_5W_{30}O_{110}]$ catalyst was calcinated in air for 3 h at 230 °C and then introduced into the reactor. The known amounts of benzene and 1-decene were introduced to the reactor according to the experimental design tests. Filtration of the reaction mixture was done after each run to remove catalyst particles. The filtrate was analyzed using an Agilent 6890 GC system equipped with an Hp-5 capillary 30 m × 530 μm × 1.5 μm nominal GC/mass.

4 ANFIS Modeling

In this modeling, the catalyst loading, catalyst weight percent, and benzene to 1-decene molar ratio were used as input, while 1-decene conversion and LAB production yield were used as output. In order to model outputs, a computer program was performed under MATLAB (version 7.7. The MathWorks Inc., USA) environment using ANFIS toolbox. In the training of the model, a "hybrid learning algorithm" was used and the number of epochs was chosen as 2000. The number of the membership function is 2 for each input. The type of the membership functions was "guss" for 1-decene conversion and "trimf" for LAB production yield.

The database to be introduced to the ANFIS was broken down randomly into two groups: training and testing. The ANFIS was trained using the training data set. The test set was used to evaluate the predictive ability of the ANFIS. Training continued as long as the computed error between the actual and predicted outputs for the test set was decreased. Typically, 75% of the data are used for training and the rest are categorized as testing. The testing set is used to evaluate the accuracy of the newly trained ANFIS by providing the ANFIS a set of data it has never seen. During the testing, the learning is turned off and the chosen data set is fed through the ANFIS. ANFIS output is collected and a report is then generated showing the testing results.

Performance efficiency of the network was evaluated using the experimental, and ANFIS estimated values using normalized mean squared error (NMSE) and R^2 (coefficient of determination) [Eqs. (1) and (2)].

$$\mathrm{NMSE} = \frac{1}{\sigma^2}\frac{1}{N}\sum_{i=1}^{N}(O_i - T_i)^2 \tag{1}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(O_i - T_i)^2}{\sum_{i=1}^{N}(O_i - T_m)^2} \tag{2a}$$

$$T_m = \frac{\sum_{i=1}^{N} O_i}{N} \tag{2b}$$

Table 1 ANFIS performance values for train and test

	NMSE		R^2	
	Train	Test	Train	Test
1-Decene conversion	0.0192	0.0184	0.99	0.994
LAB production yield	0.003	0.0056	0.997	0.995

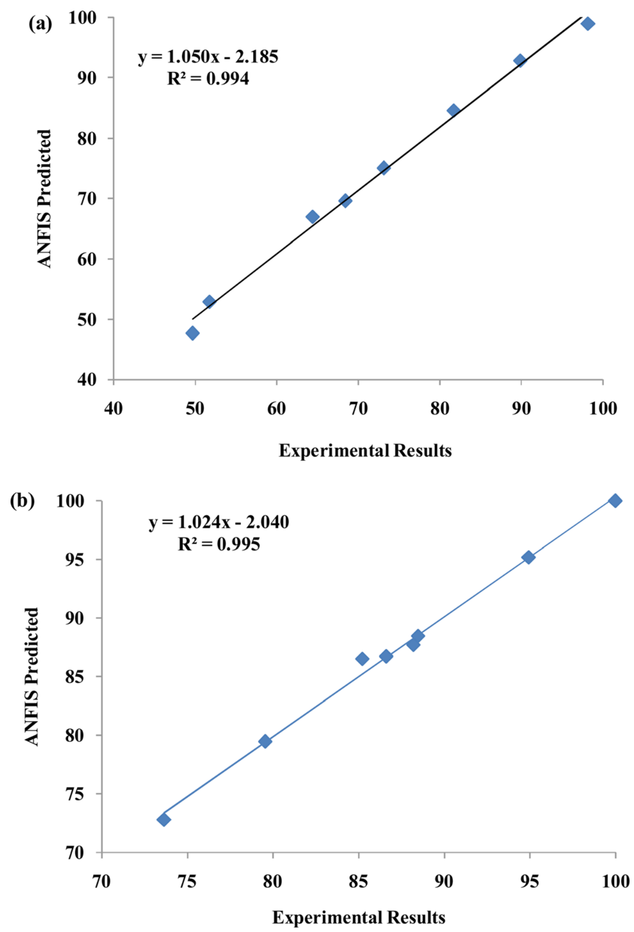

Fig. 2 ANFIS predicted values versus experimental results for testing data of (*a*) 1-decene conversion and (*b*) LAB production yield

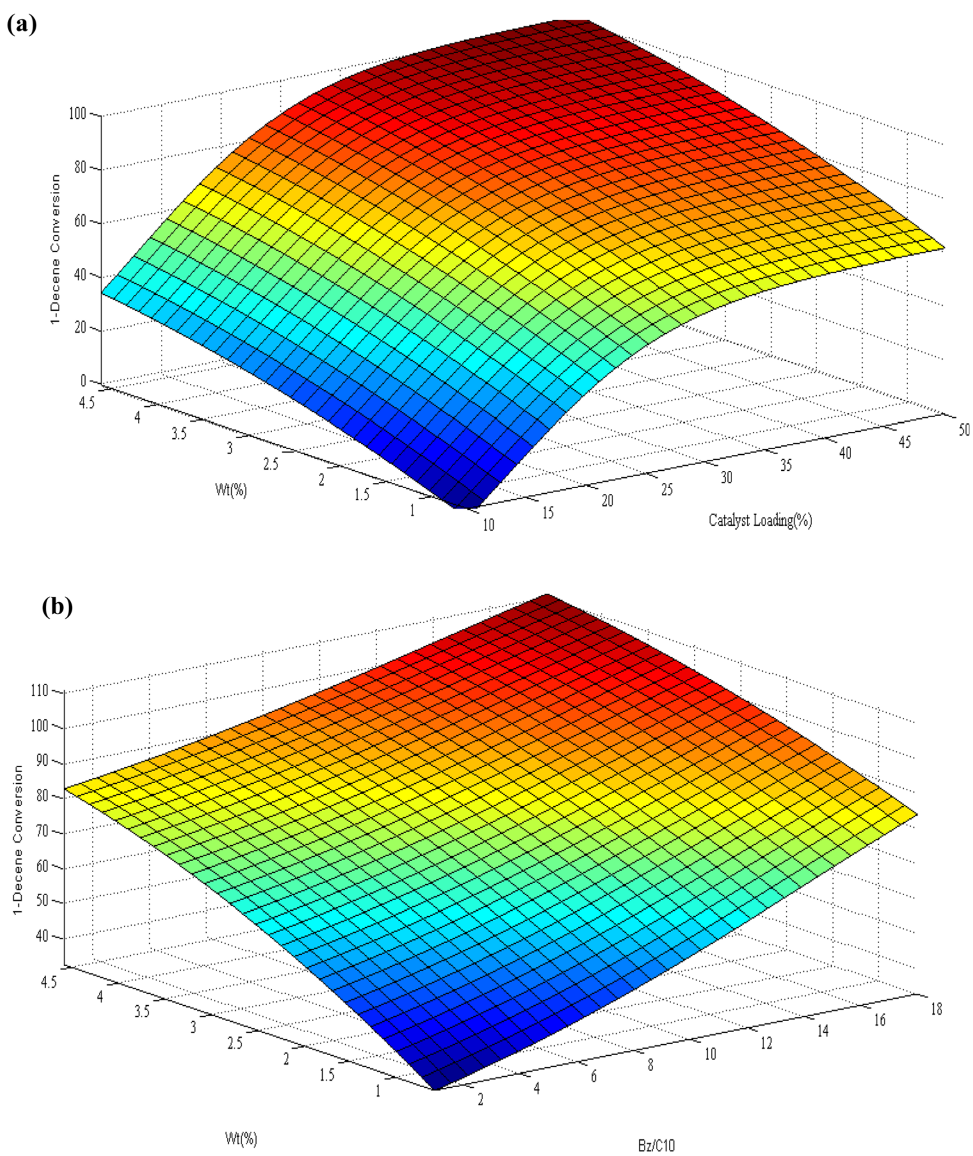

Fig. 3 Surface generated for the effects of reaction parameters on 1-decene conversion (%): (*a*) catalyst loading (%) and catalyst weight percent (wt. %) and (*b*) Bz/C_{10} molar ratio and catalyst weight percent (wt. %)

where O_i is the ith experimental value, T_i is the ith predicted value, N is the number of data, and σ^2 is the variance of experimental data [18,19].

5 Simulation Results

In this reaction, the catalyst loading was in the range of 10–40%, catalyst weight percent was in the range of 0.5–3.6 (wt. %), and benzene to 1-decene molar ratio was chosen from 5 to 17. The database containing 47 different experimental data were introduced to ANFIS.

Table 1 shows the ANFIS performance in terms of NMSE and the coefficient of determination R^2. Low value of normalized mean square error and also high R^2 of train and test shows the accuracy of ANFIS model.

The best resulted ANFIS model efficiency was evaluated using the experimental and ANFIS estimated values for 1-decene conversion and LAB production yield in training and testing data sets. From Figs. 2(*a*) and 2(*b*), the coefficients of determination were found to be 0.994 and 0.995 for 1-decene conversion and LAB production yield of testing data set, respectively. These R-squares are well close to 1 indicating superior agreement between experimental data and ANFIS predicted results.

ANFIS predicted surfaces of 1-decene conversion with catalyst loading, catalyst weight percent (wt. %), and benzene to 1-decene molar ratio are represented in Figs. 3(*a*) and 3(*b*). As indicated in this figure, increasing catalyst loading results in enhancement of 1-decene conversion. For instance, increasing catalyst loading from 10 to 50 at catalyst weight percent of 4 and Bz/C_{10} molar ratio of 9 enhances 1-decene conversion increases from 33% to about 100%. Bz/C_{10} molar ratio and catalyst weight percent have positive effects on 1-decene conversion [Figs. 3(*a*) and 3(*b*)].

The simultaneous effect of catalyst loading, catalyst weight percent, and Bz/C_{10} molar ratio on LAB production yield is shown in Figs. 4(*a*) and 4(*b*). As demonstrated in Fig. 4(*a*), increasing the catalyst loading decreases LAB production yield. Catalyst weight percent and Bz/C_{10} molar ratio tend to increase LAB production yield.

As indicated in Fig. 5, predicted 1-decene conversion using ANFIS follows experimental results in test set appropriately, and just in some points has a little deviation. It is obvious from Fig. 6

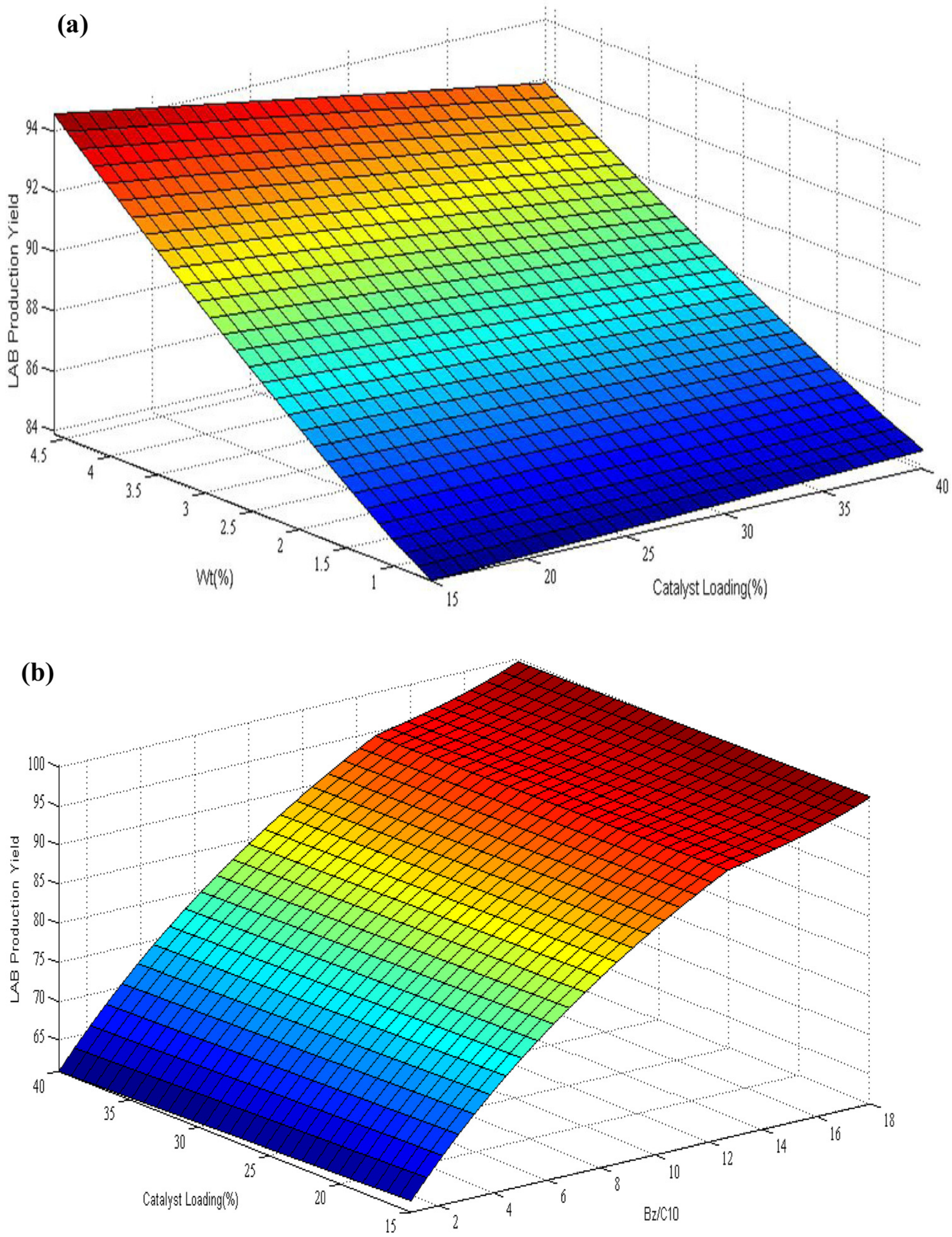

Fig. 4 Surface generated for the effects of reaction parameters on LAB production yield (%): (*a*) catalyst loading (%) and catalyst weight percent (wt. %) and (*b*) Bz/C_{10} molar ratio and catalyst loading (%)

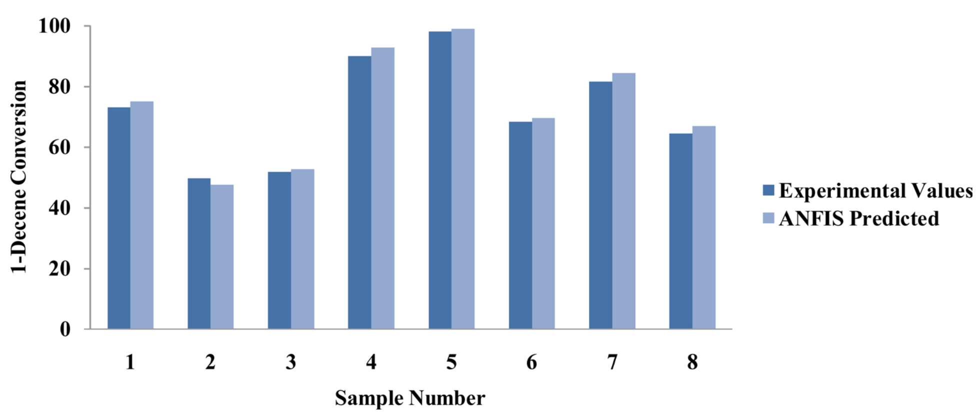

Fig. 5 ANFIS predicted and experimental values of 1-decene conversion

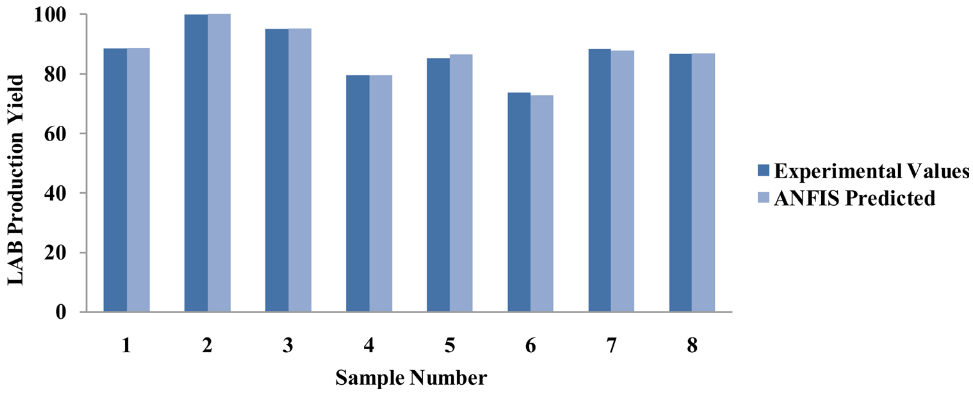

Fig. 6 ANFIS predicted and experimental values of LAB production yield

that ANFIS predicted LAB production yield and experimental results are found in a perfect match for the test data.

6 Conclusion

In this study, we applied ANFIS approach for the investigation and prediction of catalytic performance of silica-supported Preyssler nanocatalyst in the alkylation of benzene. The nanocatalyst was tested in a glass batch reactor at a constant temperature of 80 °C at different catalyst loading, Bz/C_{10} molar ratio, and catalyst weight percent. ANFIS method was applied for the modeling of experimental results and prediction of 1-decene conversion and LAB production yield. The results showed an excellent agreement between model predictions and experimental data at all the operating conditions considered in this investigation.

Catalyst loading, Bz/C_{10} molar ratio, and catalyst weight percent showed positive effects on 1-decene conversion. On the other hand, increasing the catalyst loading tends to decrease LAB production yield. Catalyst weight percent and Bz/C_{10} molar ratio tend to increase LAB production yield.

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